

**Mass Transport in Oxides For Membrane Reforming
of Methane**

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The application of mixed ionic-electronic conducting oxide ceramic membranes in electrochemical membrane reactors, such as methane reformers, is an area of great technological and commercial interest. For such application key requirements for a successful material are fast oxygen ionic diffusion and surface exchange as well as good electronic conductivity. The material must not only exhibit the appropriate transport properties and thermodynamic stability but must also withstand the mechanical stresses caused by the lattice expansion on reduction. Promising materials can be found in the perovskite-based system $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Cr}_y\text{O}_{3\pm\delta}$. The mass transport behaviour, nonstoichiometry and stability of materials with compositions $x=0.2, 0.4, 0.6, 0.8$ and $y=0.2, 0.4$ have been investigated.

The ceramic powders were prepared by the modified Pechini [1] or the conventional mixed oxide route. The materials were processed into pellets with densities $\geq 95\%$ of theoretical. The samples were pre-annealed and then diffusion annealed at temperatures between 700-1000 °C under atmospheres of dry $^{18}\text{O}_2$, H_2^{18}O and mixtures of $\text{H}_2^{18}\text{O}/\text{N}_2/\text{H}_2$ (forming gas). The ^{18}O penetration profiles were determined by secondary ion mass spectrometry (SIMS). Proton diffusion was investigated by annealing the samples under D_2O atmospheres. The variation of nonstoichiometry with oxygen activity was investigated by coulometric titration. Potentiostatic measurements were made using YSZ-based electrochemical cells [2].

The experimental ^{18}O penetration profiles were fitted to the appropriate solution of the diffusion equation [3], allowing the extraction of parameters D^* (tracer diffusion coefficient) and k (surface exchange rate constant) as summarised in figures 1 and 2. D^* was found to increase with increasing temperature and decreasing oxygen activity. These results are consistent with diffusion being proportional to the concentration of oxygen vacancies. At high $p\text{O}_2$ increasing Sr concentration increases D^* , as expected from the increase in oxygen vacancy concentration, but at more reducing conditions D^* appears to be insensitive to the Sr concentration which might indicate defect interactions when a large concentration of oxygen vacancies is present. Activation energies for D^* increase with increased Cr content, which is consistent with its expected stabilizing effect when substituted on the B-site. The surface exchange rate exhibits a far more complicated behaviour, showing dependence not only on the oxygen activity but also on the reactant gas. As the Sr content increases the materials exhibit severe mechanical instabilities. Sample quenching can cause severe cracking or even disintegration of the samples.

The studied materials exhibit very promising oxygen transport properties and thermodynamic stability under reducing conditions. Nevertheless, mechanical instabilities impose a compromise between delivered fluxes and operational feasibility.

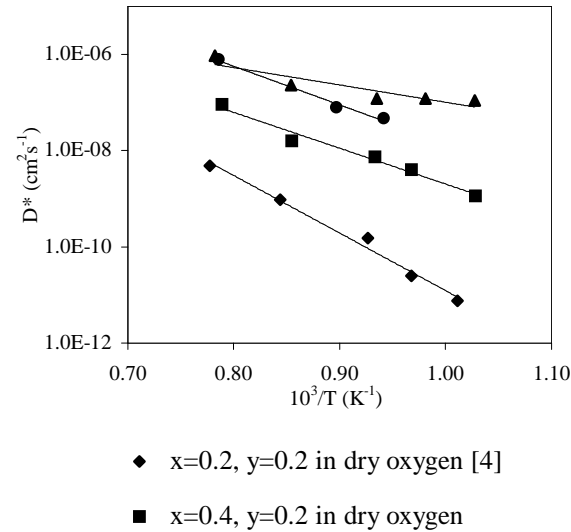


Figure 1: Arrhenius plot of the oxygen tracer diffusion coefficient in two different gas atmospheres. The straight lines are the fitted Arrhenius expressions.

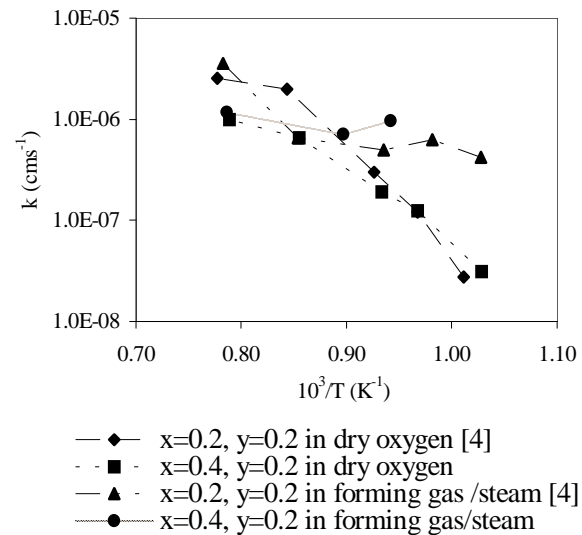


Figure 2: Arrhenius plot of the oxygen surface exchange coefficient in two different gas atmospheres. The lines are visual aids and have no theoretical significance.

References
[1] M.P. Pechini, US Pat. 3330 697 (1967)
[2] M.H.R. Lankhorst and H.J.M. Bouwmeester., J.Electrochem. Soc., Vol. 144, No.4, April 1997
[3] J. Crank, "The Mathematics of Diffusion", 2nd Edition, Clarendon Press, Oxford, 1975
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